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Synthesis and optimization of fluorine-free Y and Cu precursor solution for MOD processing of YBCO coated conductor

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Abstract

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Keywords

Synthesis, optimization, fluorine, free, precursor, solution, for, MOD, processing, YBCO, coated, conductor

Disciplines

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Synthesis and Optimization of Fluorine-Free Y & Cu Precursor Solution for MOD Processing of YBCO Coated Conductor

Jaimoo Yoo, Young-Kuk Kim, Kookchae Chung, Jaewoong Ko, Xiaolin Wang, and Shi Xue Dou

***Abstract*—MOD solutions for YBCO coated conductors were synthesized with fluorine-free Y & Cu precursor. The fluorine content in the precursor solution was significantly reduced and a fast calcination profile was realized. A crack-free & thick precursor film was successfully obtained just after less than 2 hours of calcination in wet O_2 atmosphere. Optimization of the precursor solution with Sm addition enables further improvement of thickness and uniformity of precursor films. The calcinated precursor film was successfully converted to dense and uniform YBCO film after annealing in wet Ar/O_2 atmosphere. The measured critical current value was about 273 A/cm-w ($J_c \sim 3.8$ MA/cm^2), and well-developed microstructure was confirmed. Also discussed are recent developments in the reel-to-reel processing using the precursor solution with low fluorine-content. It was shown that employing fluorine-free Y & Cu precursor solution enabled uniform and fast processing of YBCO coated conductors.**

***Index Terms*—Coated conductor, fluorine, MOD, precursor solution.**

I. Introduction

METAL-ORGANIC deposition (MOD) of $YBa_2Cu_3O_{7-x}$ (YBCO)-based high temperature superconducting coated conductors is attracting much interest because of its potential for scale-up and cost-effectiveness [1]–[3]. Generally, MOD is a non-vacuum chemical solution deposition process capable of being scaled to industrial levels. In particular, YBCO thin films with high critical current density ($J_c > 1$ MA/cm^2) can be routinely fabricated by MOD-TFA process using trifluoroacetate (TFA)-based precursor solution [4]. Therefore, fabrication of YBCO-based coated conductors on the biaxially textured, polycrystalline substrates using MOD technique is a topic of technological importance.

One of the most important issues in the MOD-processing of YBCO coated conductor is synthesis of MOD precursor solution. Metal-TFA salts in the precursor solution of the conventional MOD-TFA process generate large amount of HF gas during the calcination step. As a result of this, long processing time is required to fabricate crack-free precursor film compared with conventional MOD process for ceramic film, and thickness of precursor film is limited to low values after single coating and calcination [5], [6]. Then, scale-up of MOD-TFA process is limited. The large HF gas generation during the calcination step in MOD-TFA process can be attributed to the large amount of fluorine contained in the precursor solution [6]. In order to shorten the processing time and to obtain thick and dense YBCO layers, reduction of fluorine content in the precursor solution is required. Then, many efforts have been made to enhance the processing by modification of precursor solution [6]–[12]. Dawley *et al.* reported 1.5 μm thick YBCO film on $LaAlO_3$ single crystal by adding diol or triol to increase the viscosity [7]. In addition to this, the improvement in processing time and thickness of precursor films were done by reducing fluorine content in the precursor solution [9]–[11]. Recently, a precursor solution developed by ISTEC (Japan) provided YBCO film with high critical current density of 692 A/cm after multiple coating and calcination [12].

In this study, a new precursor solution for MOD processing was synthesized to improve the processing and thickness of YBCO films. The amount of total fluorine in the newly synthesized precursor solution was significantly reduced compared with that of conventional all TFA-based precursor solution. Accordingly, a fast calcination profile was applied to reduce the processing time. We report here on successful MOD fabrication of high performance YBCO coated conductors using precursor solution with low fluorine content.

II. Experimentals

A. Synthesis of Precursor Solution

A MOD precursor solution with low fluorine content was synthesized by dissolving metal precursors into methanol. fluorine-free yttrium and copper acetated-based metal salts were employed as yttrium and copper precursors. Those metal acetate-based salts were prepared by mixing metal acetate and proper chelating agents. In addition to this, barium trifluoroacetate (TFA) salt was used as a barium precursor to synthesize the new precursor solution. The synthesized precursor solution was condensed to control the viscosity. In addition to this, samarium precursor was added to the synthesized precursor solution. The amount of samarium in the precursor solution is less than 10% of yttrium content.

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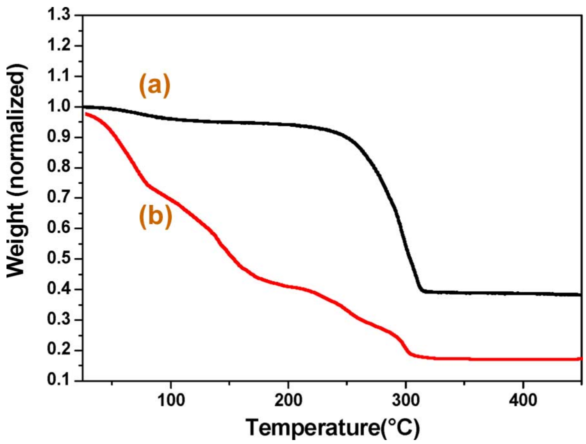

Fig. 1. Thermogravimetric analysis of precursor solutions: (a) all TFA solution, (b) F-free Y & Cu solution.

B. Preparation of YBCO Coated Conductors

Buffered Ni-W tapes ($CeO_2/YSZ/CeO_2$/Ni-W) supplied from Korea Electrotechnology Research Institute (KERI) were employed as substrates for YBCO coated conductor. Synthesized precursor solution was deposited on the surface of buffered metal tape by slot die coating method. Deposited gel film was calcined in humidified oxygen atmosphere and annealed in humidified Ar/O_2 mixed gas.

III. Results and Discussions

A. Synthesis and Optimization of F-Free Y & Cu Solution

Since the F-free Y & Cu precursor solution was synthesized by dissolving F-free yttrium and copper precursor into methanol with barium TFA salt, the total content of fluorine in the precursor solution is only 30% of that for conventional MOD-TFA precursor solution synthesized with metal-TFA salts (hereafter referred as all TFA solution). In order to investigate the weight change during calcination process of the F-free Y & Cu precursor solution, thermogravimetric analysis (TGA) of precursor solution was performed. TGA data of both all TFA solution and F-free Y & Cu solution were measured independently to compare the pyrolysis behavior (Fig. 1).

TGA data of all TFA solution shows abrupt change of weight in the temperature range of $250 \sim 300^{\circ}C$. The abrupt weight change can be related to large amount of HF gas generation during the calcination step. As a result of this, there will be many pores and cracks in the calcined precursor film and calcination of crack-free precursor film requires slow heating and long calcination time. Contrary to this, pyrolysis behavior of F-free Y & Cu precursor solution shows gradual change of weight during the heating process in the wide temperature range [Fig. 1(b)]. This implies that thick precursor films without cracks are expected to be fabricated by applying F-free Y & Cu precursor solution even after fast heating.

Since the F-free Y & Cu solution was expected to be suitable for fast calcination profile, the calcination was performed by heating gel film to 400°C in wet O_2 atmosphere with the rate of $5^{\circ}C/min$. Less than 2 hours are required to finish calcination process including cooling. As shown in Fig. 2, the

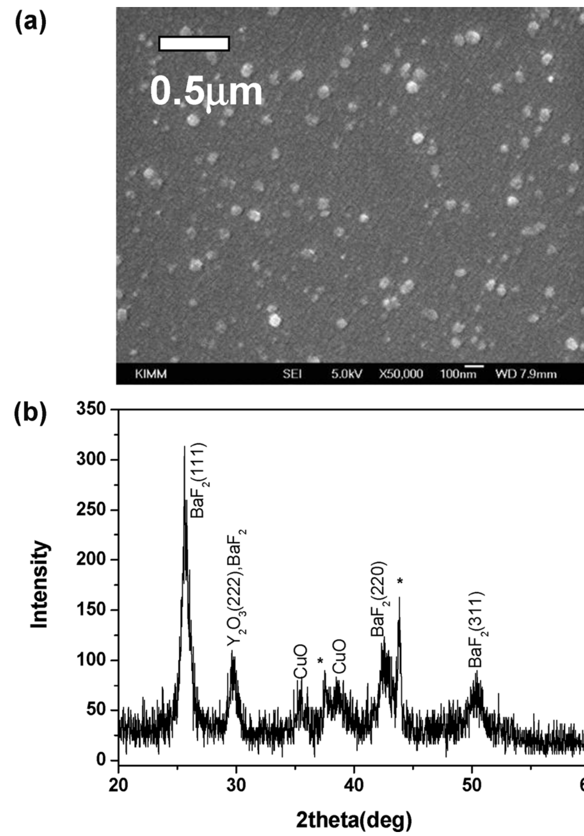

Fig. 2. (a) Surface and (b) X-ray diffraction profile of calcined precursor film.

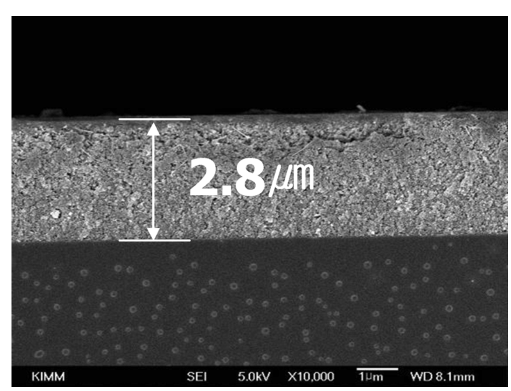

Fig. 3. Fractured surface of a precursor film prepared with slot die coating method and F-free Y & Cu solution with high viscosity ($\eta = 120$ cP).

precursor film after calcination shows dense and crack-free microstructure with uniform distribution of BaF_2, CuO and Y_2O_3, which is consistent with the calcined film prepared by all TFA solution [4].

Thickness of as-calcined precursor film prepared with F-free Y & Cu precursor solution was measured. By increasing solution viscosity, thicker precursor film was expected to be formed after calcination. In this study, a slot-die coating was applied to obtain uniform and thick precursor film. Fig. 3 shows a fractured surface of precursor film prepared by slot-die coating of F-free Y & Cu precursor solution with high viscosity (viscosity $=$ 120 cP). Up to 2 μm, crack-free & thick precursor film can be formed by slot-die coating. However, it still has problems when

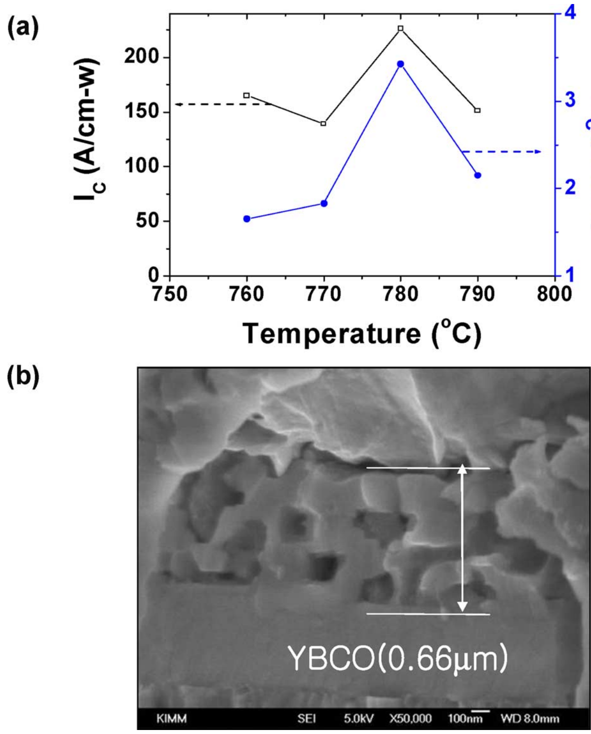

Fig. 4. (a) Variation of critical current and critical current density with respect to annealing temperatures and (b) cross-sectional view of YBCO coated conductors annealed at 780°C.

annealing these thick films. Calcined precursor film (slot-die coated) used in this study is $\sim 2.0\ \mu$m.

In addition to this, samarium doped F-free Y & Cu precursor solution was synthesized. Interestingly, viscosity of precursor solution was greatly improved by samarium addition from 70 cP to 260 cP. Synthesized precursor solution was deposited on $CeO_2/YSZ/CeO_2$ buffered Ni-W alloy tape by slot-die coating and subsequent calcination. Calcined precursor film was converted to YBCO after annealing in humid Ar/O_2 atmosphere at the range of 760 $\sim$ 790°C. DC 4-probe measurement shows that critical current of YBCO coated conductors were more than 100 A/cm after annealing at the range of 760 $\sim$ 790°C [Fig. 4(a)]. In particular, YBCO coated conductor annealed at 780°C shows high critical current (I_c) of 226 A/cm. The thickness of annealed YBCO film was estimated to be $\sim$ 0.66 μm from cross-sectional observation and the calculated critical current density (J_c) of YBCO layer was $\sim$ 3.4 MA/cm^2 [Fig. 4(b)].

In addition, a modified temperature profile was applied to the calcination of F-free Y & Cu precursor solution with samarium addition coated on buffered Ni-W alloy tape. After annealing at 780°C, surface of YBCO layer shows dense microstructure with small number of pores [Fig. 5(a)]. Thickness of YBCO layer was measured to be about 0.72 μm from the observation of fractured surface [Fig. 5(b)]. Critical current measured by transport method was $I_c = 273$ A/cm (with 1.5 mm wide bridge) and $J_c = 3.8$ MA/cm^2.

Hence, it was shown that YBCO film with high J_c can be fabricated using F-free Y & Cu precursor solution with samarium addition.

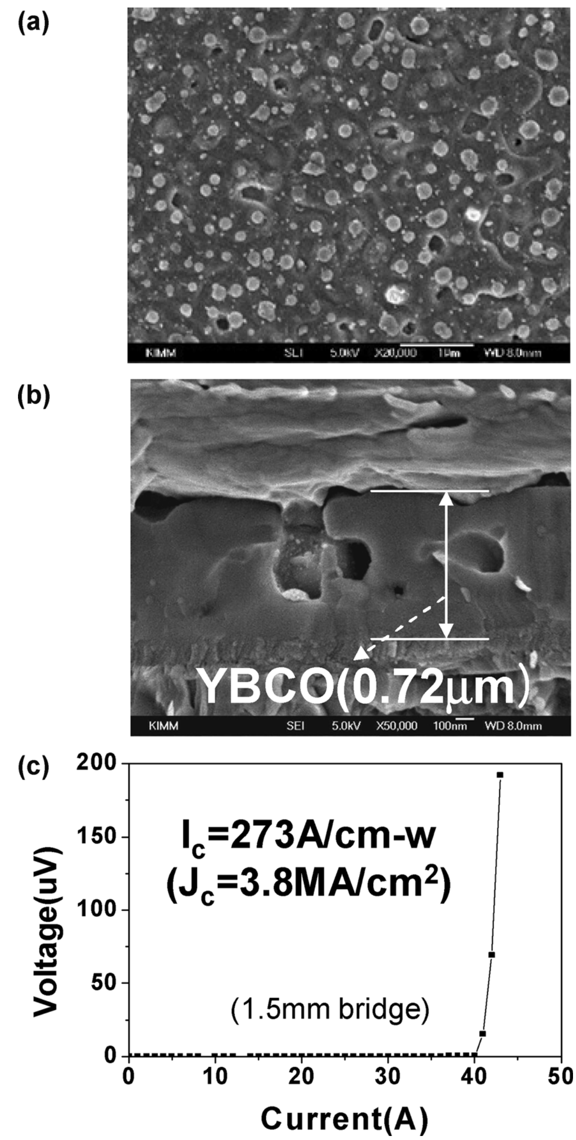

Fig. 5. Microstructure and critical current of YBCO coated conductors calcined with modified temperature profile: (a) surface, (b) cross-sectional view, (c) critical current measurement.

B. Reel-to-Reel Processing of YBCO Coated Conductors

A reel-to-reel slot-die coating and calcination system equipped with precise control of slot die coating parameters was installed in KIMM and it enables continuous coating and calcination with speed of 5 m/h is possible. In order to maintain uniformity of gas flow and temperature in continuous annealing process, a reel-to-reel annealing system equipped with vertical gas flow control system and 9-zone control furnace was designed and installed.

A 42 cm-long YBCO coated conductor was fabricated by reel-to-reel processing of YBCO coated conductors using F-free Y & Cu precursor solution with samarium addition. Prior to slot-die coating of precursor solution, the surface of buffered substrate was thermally treated in oxygen atmosphere to improve wettability of solution and uniformity of coating. Precursor solution was deposited on a buffered Ni-W substrate with

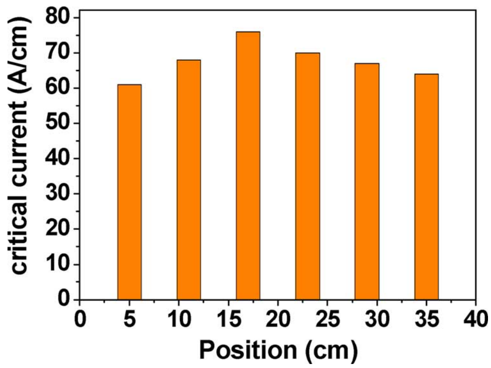

Fig. 6. Variation of critical current with respect to position in the reel-to-reel processed YBCO coated conductor.

slot-die coating method and calcined continuously. After calcination, the precursor film was annealed at 780°C using reel-to-reel annealing facility. Measured critical current of the YBCO coated conductor was ~63 A/cm (end-to-end) and estimated critical current density was 0.9 MA/cm^2 (Fig. 6). Further modification and optimization of reel-to-reel MOD processing is in progress to improve critical current of coated conductor.

IV. Summary

In order to reduce fluorine content in the precursor solution, F-free Y & Cu precursor solution was synthesized. A crack-free 2.8 μm-thick precursor film was fabricated through slot-die coating & fast calcinations process. Less than 2 hours are required to finish the calcination process. YBCO coated conductor deposited on buffered Ni-W alloy tape using F-free Y & Cu precursor solution with samarium addition shows critical current of 273 A/cm ($J_c = 3.8$ MA/cm^2) after single coating. In addition to this, 42 cm-long YBCO coated conductor was fabricated by reel-to-reel continuous processing with F-free Y & Cu precursor solution with Sm addition. In this study, it was shown that employing F-free Y & Cu precursor solution is expected to improve fast processing of YBCO coated conductors with high critical current. Further optimization of precursor solution and reel-to-reel continuous processing is in progress.

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